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(54) **A method of aluminising a superalloy**

Verfahren zur Aluminisierung einer Superlegierung

Procédé d'aluminisation d'un superalliage

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Description

[0001] The present invention relates to the application of aluminide coatings to superalloys, in particular single crystal superalloys.

[0002] Single crystal superalloys have been developed for gas turbine engine turbine blades and turbine vanes to provide optimum high temperature strength for the turbine blades and turbine vanes. However, the changes in the composition of the single crystal superalloys compared to the composition of earlier superalloys has resulted in these single crystal superalloys experiencing increased surface degradation. In addition there is a requirement for the turbine blades and turbine vanes to have longer service lives. Thus these single crystal superalloy turbine blades and turbine vanes are not providing satisfactory service lives due to their degradation by corrosion and oxidation.

[0003] These single crystal superalloys generally comprise rhenium, for example 2 to 8 wt% together with relatively high levels of tungsten and tantalum to obtain the high temperature strength characteristics. These single crystal superalloys are very strong at high temperatures due to the benefits of the rhenium, tungsten and tantalum.

[0004] In order to increase the service lives of single crystal turbine blades and turbine vanes it is desirable to protect the surface of the single crystal turbine blades or turbine vanes with a protective coating. One known type of protective coating which is commonly applied to turbine blades and turbine vanes is a platinum aluminide coating. The platinum aluminide coatings are applied by firstly coating the turbine blades, or turbine vanes, with platinum and by secondly aluminising the platinum coated turbine blades, or turbine vanes, using an aluminising processes. The aluminising process may be by pack aluminising process, by the out of pack gas phase aluminising process, by chemical vapour deposition or by other processes well known to those skilled in the art.

[0005] However, it has been found that if high rhenium containing single crystal superalloy turbine blades, or turbine vanes, are platinum aluminised using conventional processes topologically close packed phases are formed at the interface between the coating and the single crystal superalloy. High rhenium containing single crystal superalloys are those containing more than 4 wt% rhenium. These topologically close packed phases are formed directly following aluminising or following exposure to high temperatures. The topologically close packed phases contain high levels of rhenium, tungsten and chromium compared to the single crystal superalloy, and are more easily formed with increasing levels of rhenium in the single crystal superalloy. The topologically close packed phases increase in amount with increasing time at high temperatures. The topologically close packed phases adversely effect the mechanical properties of the single crystal superalloy. Thus it is not possible to use a conventional platinum aluminide coat-

ing to increase the resistance to degradation of a high rhenium containing single crystal superalloy without decreasing the mechanical properties of the single crystal superalloy.

5 [0006] Other types of protective coatings which are commonly applied to turbine blades and turbine vanes are aluminide-silicide coatings, platinum aluminide-silicide coatings, simple aluminide coatings and any other suitable aluminide coatings.

10 [0007] The aluminide coatings are applied using an aluminising process, by the out of pack gas phase aluminising process, by the pack aluminising process, by chemical vapour deposition or other processes well known to those skilled in the art.

15 [0008] One method of producing aluminide-silicide coatings is by depositing a silicon filled organic slurry on a superalloy surface and then pack aluminising as described in US4310574. The aluminium carries the silicon from the slurry with it as it diffuses into the superalloy. Another method of producing aluminide-silicide coatings is by depositing a slurry containing elemental aluminium and silicon metal powders to a superalloy surface and then heating to above 760 degrees C to melt the aluminium and silicon in the slurry, such that they react with the superalloy and diffuse into the superalloy. A further method of producing aluminide-silicide coatings is by repeatedly applying the aluminium and silicon containing slurry and heat treating as described in US5547770. Another method of producing aluminide-silicide coatings is by applying a slurry of an eutectic aluminium-silicon or a slurry of elemental aluminium and silicon metal powders to a superalloy surface and diffusion heat treating to form a surface layer of increased thickness and reduced silicon content, and a layering layer which comprises alternate continuous interleaved layers of aluminide and silicide phases and a diffusion interface layer on the superalloy as described in published European patent application No. 0619856A.

30 [0009] One method of producing the platinum aluminide-silicide coatings is by coating the superalloy of the turbine blades, or turbine vanes, with platinum, then heating to diffuse the platinum into the turbine blade and then simultaneously diffusing aluminium and silicon from the molten state into the platinum enriched turbine blade as described in published International patent application No. WO95/23243A. Another method of producing platinum aluminide-silicide coatings is by coating the superalloy turbine blades with platinum, then heat treating to diffuse the platinum into the turbine blade, a silicon layer is applied and is then aluminised as described in published European patent application No. 0654542A. It is also possible to diffuse the silicon into the turbine blade with the platinum as described in EP0654542A. A further method of producing platinum aluminide-silicide coatings is by electrophoretically depositing platinum-silicon powder onto the turbine blades, heat treating to diffuse platinum and silicon into the turbine blades, electrophoretically depositing aluminium and chromium

powder and then heat treating to diffuse the aluminium and chromium into the turbine blades as described in US5057196.

[0010] It has been found that if high rhenium containing single crystal superalloy turbine blades, or turbine vanes, are coated with platinum aluminide-silicide coatings using the method described in WO95/23243A that topologically close packed phases are formed at the interface between the coating and the single crystal superalloy. It is believed that if high rhenium containing single crystal superalloy turbine blades, or turbine vanes, are coated with platinum aluminide-silicide coatings by the other methods described that topologically close packed phases will be formed.

[0011] It has also been found that if high rhenium containing single crystal superalloy turbine blades, or turbine vanes, are coated with aluminide-silicide coatings using the method described in US5547770 that topologically close packed phases are formed at the interface between the coating and the single crystal superalloy. It is believed that if high rhenium containing single crystal superalloy turbine blades, or turbine vanes, are coated with aluminide-silicide coatings by any of the other suitable methods described that topologically close packed phases will be formed.

[0012] We believe that it is the high rhenium content of the single crystal superalloy which is responsible for forming the topologically close packed phases and that these phases will be formed during simple aluminising.

[0013] Thus additionally it is not possible to use platinum aluminide-silicide coatings, aluminide-silicide coatings or simple aluminide coatings to increase the resistance to degradation of a high rhenium containing single crystal superalloy without decreasing the mechanical properties of the single crystal superalloy.

[0014] EP0784104A discloses a single crystal superalloy which has a platinum aluminide coating formed by depositing a layer of platinum onto the single crystal superalloy. EP0784104A has a priority date of 22 December 1995, a filing date of 10 December 1996 and a publication date of 16 July 1997. The single crystal superalloy is subsequently heated to diffuse the platinum into the single crystal superalloy and then the single crystal superalloy is aluminised to form a platinum aluminide protective coating or a bond coating for a thermal barrier coating.

[0015] EP0545661A discloses a high rhenium containing single crystal superalloy which has an aluminide coating formed by aluminising. Prior to aluminising carbon is deposited onto the high rhenium containing single crystal superalloy and the carbon is reacted with the rhenium to form carbides to prevent the formation of topologically close packed phases.

[0016] The present invention seeks to provide a method of aluminising a high rhenium containing single crystal superalloy which overcomes the above mentioned problem.

[0017] Accordingly the present invention provides a

method of aluminising a high rhenium containing superalloy substrate, the high rhenium containing superalloy substrate comprises at least 3.5wt% rhenium, the method comprising the steps of:

- (a) modifying the surface of the high rhenium containing superalloy substrate, by applying a layer of chromium or cobalt to the surface of the high rhenium containing superalloy substrate and heat treating to diffuse the chromium or cobalt into the high rhenium containing superalloy substrate to reduce the rhenium content of the surface of the high rhenium containing superalloy substrate, and
- (b) aluminising the high rhenium containing superalloy substrate to form an aluminide coating. The essential features of the method are defined in claim 1. Preferred embodiments are defined in claims 2 to 22. A product obtainable by the method according to claim 1 to 22 is claimed in claim 23.

[0018] The chromium or cobalt modifies the diffusion characteristics to reduce the formation of the regions of high rhenium content. The chromium or cobalt are metals compatible with the superalloy.

[0019] Step (a) may comprise applying the chromium or cobalt to the high rhenium containing superalloy substrate by electroplating, sputtering, pack diffusion, out of pack diffusion, chemical vapour deposition or physical vapour deposition.

[0020] The invention is particularly applicable to platinum aluminide coatings, platinum aluminide-silicide coatings and aluminide-silicide coatings, but is generally applicable to all aluminide coatings on high rhenium containing superalloy substrates.

[0021] The present invention will be more fully described by way of examples with reference to the accompanying drawings, in which:-

[0022] Figure 1 is a cross-sectional view through a prior art platinum aluminide coating on a low rhenium containing single crystal superalloy.

[0023] Figure 2 is a cross-sectional view through a prior art platinum aluminide coating on a high rhenium containing single crystal superalloy.

[0024] Figure 3 is a cross-sectional view through the prior art platinum aluminide coating on a high rhenium containing single crystal superalloy after ageing at a high temperature.

[0025] Figure 4 is cross-sectional view through a chromium modified platinum aluminide coating according to the present invention on a high rhenium containing single crystal superalloy.

[0026] Figure 5 is a cross-sectional view through a cobalt modified platinum coating according to the present invention on a high rhenium containing single crystal superalloy.

[0027] Figure 6 is a cross-sectional view through a cobalt modified platinum coating according to the present invention on a high rhenium containing single crystal su-

peralloy after ageing at a high temperature.

[0028] In conventional, prior art, platinum aluminising process for a single crystal superalloy the single crystal superalloy is electroplated with a layer of platinum, and the platinum plated single crystal superalloy is heat treated in a vacuum to diffuse the platinum into the single crystal superalloy. The heat treated, platinum plated single crystal superalloy is aluminised using pack aluminising, out of contact gas phase aluminising, chemical vapour deposition or other suitable process. The aluminised, diffused, platinum plated single crystal superalloy is then heat treated in a protective atmosphere to optimise the platinum aluminide coating microstructure and composition and to maximise the mechanical properties of the single crystal superalloy.

[0029] During the heat treatment to diffuse the platinum into the single crystal superalloy, after deposition of the platinum layer on the single crystal superalloy, diffusion occurs between the platinum and the single crystal superalloy to form a surface layer containing platinum, nickel and other superalloy elements. The heat treatment diffusion step is of sufficient time and temperature to ensure that a suitable composition is attained in the diffused platinum layer so that the required platinum aluminide coating is obtained following the aluminising and heat treatment process steps. A conventional platinum aluminide coating 12 on a single crystal superalloy substrate 10 is shown in figure 1.

[0030] However, when a high rhenium containing single crystal superalloy is heat treated after deposition of the platinum layer, the inward diffusing platinum produces a zone enriched in rhenium and other refractory elements, for example tungsten and chromium, in front of it. In the subsequent aluminising and heat treatment process steps, to produce the required platinum aluminide coating, the zone enriched in rhenium and other refractory elements is retained within the coating. This zone enriched in rhenium and other refractory elements acts as an initiator for the formation of the topologically close packed phases. The topologically close packed phases are needle shaped.

[0031] The topologically close packed phases form at the interface between the high rhenium containing single crystal superalloy and the platinum aluminide coating. The topologically close packed phases form either after all the process steps for forming the platinum aluminide or following exposure of the platinum aluminide and high rhenium containing single crystal superalloy to high temperatures. The topologically close packed phases contain high levels of rhenium, compared to the single crystal superalloy, and are more easily formed as the rhenium content of the single crystal superalloy increases. The topologically close packed phases effect the performance of the single crystal superalloy component, because the topologically close packed phase region has lower creep strength than the single crystal superalloy. It will therefore reduce the effective load bearing cross-section of the turbine blade, or turbine vane.

[0032] A conventional platinum aluminide coating 22 on a high rhenium containing single crystal superalloy substrate 20 after ageing at high temperature is shown in figure 3. Additionally topologically close packed phases 24 are present at the interface between the platinum aluminide coating 22 and the high rhenium containing single crystal superalloy substrate 20.

[0033] The present invention modifies the surface of a high rhenium containing single crystal superalloy in a manner which allows the platinum layer to diffuse into the high rhenium containing single crystal superalloy, in the following heat treatment step, without the formation of the zone enriched in rhenium and other refractory elements in front of the platinum. The subsequent aluminising and heat treatment steps produce a platinum aluminide coating without topologically close packed phases at the interface between the high rhenium containing single crystal superalloy and the platinum aluminide.

EXAMPLE 1

[0034] A sample of a conventional low rhenium containing nickel based single crystal superalloy, for example CMSX4, was platinum aluminised according to the following procedure.

[0035] CMSX4 is produced by the Cannon-Muskegon Corporation of 2875 Lincoln Street, Muskegon, Michigan MI 49443-0506, USA. CMSX4 has a nominal composition of 6.4 wt% tungsten, 9.5 wt% cobalt, 6.5 wt% chromium, 3.0 wt% rhenium, 5.6 wt% aluminium, 6.5 wt% tantalum, 1.0 wt% titanium, 0.1 wt% hafnium, 0.6 wt% molybdenum, 0.006 wt% carbon and the balance is nickel.

[0036] A platinum layer was deposited onto the low rhenium containing nickel based single crystal superalloy by electroplating, sputtering, CVD, PVD or other suitable method to a thickness in the range 2.5 to 12.5 micrometers (μm) and was heat treated in a vacuum, or a protective atmosphere, for 1 to 4 hours at a temperature within the range 900°C to 1150°C to diffuse the platinum into the low rhenium containing nickel based single crystal superalloy. More specifically the platinum was deposited by electroplating to a thickness of 7 micrometers (μm) and was heat treated in a vacuum for 1 hour at 1100°C.

[0037] Then the diffused platinum plated low rhenium containing nickel based single crystal superalloy was aluminised by pack aluminising, out of pack aluminising or CVD aluminising within the temperature range 700°C to 1150°C. More specifically the diffused platinum plated low rhenium containing nickel based single crystal superalloy was pack aluminised for 20 hours at 875°C.

[0038] Then the platinum aluminised low rhenium containing nickel based single crystal superalloy was heat treated in a vacuum, or a protective atmosphere, for 1 hour at 1100°C and 16 hours at 870°C.

[0039] A low rhenium containing nickel based single

crystal superalloy with a platinum aluminide coating as shown in figure 1 was produced. Samples of the low rhenium containing nickel based single crystal superalloy with a platinum aluminide coating were exposed in cyclic oxidation tests for 200 hours at 1050°C and for 100 hours at 1100°C and no topologically close packed phases were found beneath the platinum aluminide coating in either case.

EXAMPLE 2

[0040] Samples of a high rhenium containing nickel based single crystal superalloy, for example CMSX10, were platinum aluminised according to the following procedure. The rhenium containing nickel based single crystal superalloy is known as CMSX 10 and is produced by the Cannon-Muskegon Corporation of 2875 Lincoln Street, Muskegon, Michigan MI 49443-0506, U. S.A.

This alloy has a nominal composition range of 3.5 to 6.5 wt% tungsten, 2.0 to 5.0 wt% cobalt, 1.8 to 3.0 wt% chromium, 5.5 to 6.5 wt% rhenium, 5.3 to 6.5 wt% aluminium, 8.0 to 10.0 wt% tantalum, 0.2 to 0.8 wt% titanium, 0.25 to 1.5 wt% molybdenum, 0 to 0.03 wt% niobium, 0.02 to 0.05 wt% hafnium, 0 to 0.04 wt% carbon and a balance of nickel.

[0041] A platinum layer was deposited onto the samples of the high rhenium containing nickel based single crystal superalloy by electroplating, sputtering, CVD, PVD or other suitable method to a thickness in the range 2.5 to 12.5 micrometers (μm) and was heat treated in a vacuum, or protective atmosphere, for 1 to 4 hours at a temperature within the range 900°C to 1150°C to diffuse the platinum into the high rhenium containing nickel based single crystal superalloy. More specifically the platinum layer was deposited by electroplating to a thickness of 7 micrometers (μm) and was heat treated for 1 hour at 1100°C.

[0042] Then the diffused platinum coated samples of high rhenium containing nickel based single crystal superalloy were aluminised using pack aluminising, out of pack aluminising or CVD aluminising within the temperature range 700°C to 1150°C. More specifically the diffused platinum coated high rhenium containing nickel based single crystal superalloy samples were aluminised using out of pack aluminising for 6 hours at 1080°C.

[0043] Then the platinum aluminised samples of high rhenium containing nickel based single crystal superalloy was heat treated in a protective atmosphere for 1 hour at 1100°C and 16 hours at 870°C.

[0044] A high rhenium containing nickel base single crystal single crystal superalloy substrate 20 with a platinum aluminide coating 22 is shown in figure 2.

[0045] One of the samples was examined and zones containing topologically close packed phases were found to a depth of 30 micrometers (μm) at the interface between the platinum aluminide and the rhenium con-

taining nickel based single crystal superalloy.

[0046] Samples of the high rhenium containing nickel based single crystal superalloy with a platinum aluminide coating were exposed in cyclic oxidation tests for 100 hours at 1100°C, and subsequent examination revealed growth of the topologically close packed phases to form a continuous zone with a depth of 160 micrometers (μm) at the interface between the platinum aluminide and the rhenium containing nickel based single crystal superalloy.

[0047] A high rhenium containing nickel based single crystal superalloy substrate 20 with a platinum aluminide coating 22 after ageing at a temperature of 1100°C is shown in figure 3, which has topologically close packed phases 24.

EXAMPLE 3

[0048] Samples of a high rhenium containing nickel based single crystal superalloy were platinum aluminised according to the following procedure. The high rhenium containing nickel based single crystal superalloy is known as CMSX 10 and is produced by the Cannon-Muskegon Corporation of 2875 Lincoln Street, Muskegon, Michigan MI 49443-0506, U.S.A. This alloy has a nominal composition as discussed above.

[0049] Samples of the high rhenium containing nickel based single crystal superalloy had there surfaces modified by formation of a chromium enriched surface layer using electroplating, sputtering, CVD, PVD or other suitable methods plus a diffusion heat treatment in vacuum, or protective atmosphere. More specifically the chromium enrichment was accomplished by out of pack chromising for 3 hours at a temperature of 1100°C to form a chromium enriched surface layer 15 micrometers (μm) in depth.

[0050] A platinum layer was deposited onto the chromium enriched high rhenium containing nickel based single crystal superalloy by electroplating, sputtering, CVD, PVD or other suitable method to a thickness in the range 2.5 to 12.5 micrometers (μm) and was heat treated in a vacuum, or protective atmosphere, for 1 to 4 hours at a temperature within the range 900°C to 1150°C to diffuse the platinum into the high rhenium containing nickel based single crystal superalloy. More specifically the platinum layer was deposited by electroplating to a thickness of 7 micrometers (μm) and was heat treated for 1 hour at 1100°C.

[0051] Then the chromised, diffused, platinum coated high rhenium containing nickel based single crystal superalloy was aluminised by pack aluminising, out of pack aluminising or CVD aluminising within the temperature range 700°C to 1150°C. More specifically the chromised, diffused, platinum coated high rhenium containing nickel based single crystal superalloy samples were aluminised using out of pack aluminising for 6 hours at 1080°C.

[0052] The platinum aluminised chromised high rhe-

nium containing nickel based single crystal superalloy was heat treated for 1 hour at 1100°C plus 16 hours at 870°C.

[0053] One of the samples was examined and no zones containing topologically close packed phases were found at the interface between the platinum aluminide and the high rhenium containing nickel based single crystal superalloy.

[0054] Some of the samples were exposed to an oxidising environment for 100 hours at 1100°C, and subsequent examination revealed no topologically close packed phases at the interface between the platinum aluminide and the high rhenium containing nickel based single crystal superalloy.

[0055] A high rhenium containing nickel base single crystal single crystal superalloy substrate 30 with a chromium modified platinum aluminide coating 32 is shown in figure 4.

EXAMPLE 4

[0056] Samples of a high rhenium containing nickel based single crystal superalloy was platinum aluminised according to the following procedure. The high rhenium containing nickel based single crystal superalloy is known as CMSX 10 and is produced by the Cannon-Muskegon Corporation of 2875 Lincoln Street, Muskegon, Michigan MI 49443-0506, U.S.A. This alloy has a nominal composition as discussed above.

[0057] Samples of the high rhenium containing nickel based single crystal superalloy had there surfaces modified by formation of a cobalt enriched surface layer using electroplating, sputtering, CVD, PVD or other suitable methods plus a diffusion heat treatment in vacuum, or protective atmosphere. A cobalt layer was deposited onto the high rhenium containing single crystal superalloy by electroplating, sputtering, CVD, PVD or other suitable method to a thickness of 2.5 to 12.5 micrometers (μm) and was heat treated in a vacuum, or protective atmosphere, for 1 to 4 hours at a temperature within the range 900°C to 1150°C.

[0058] More specifically the cobalt layer was deposited onto the high rhenium containing nickel based single crystal superalloy by electroplating to a thickness of 7 micrometers (μm) and was heat treated in a vacuum for 1 hour at 1100°C.

[0059] A platinum layer was deposited onto the cobalt enriched high rhenium containing nickel based single crystal superalloy by electroplating, sputtering, CVD, PVD or other suitable method to a thickness in the range 2.5 to 12.5 micrometers (μm) and was heat treated in a vacuum, or protective atmosphere, for 1 to 4 hours at a temperature within the range 900°C to 1150°C to diffuse the platinum into the high rhenium containing nickel based single crystal superalloy. More specifically the platinum layer was deposited by electroplating to a thickness of 7 micrometers (μm) and was heat treated for 1 hour at 1100°C.

[0060] Then the cobalt enriched, diffused, platinum coated high rhenium containing nickel based single crystal superalloy was aluminised by pack aluminising, out of pack aluminising or CVD aluminising within the temperature range 700°C to 1150°C. More specifically the cobalt enriched, diffused, platinum coated high rhenium containing nickel based single crystal superalloy samples were aluminised using out of pack aluminising for 6 hours at 1080°C.

[0061] The platinum aluminised cobalt enriched high rhenium containing nickel based single crystal superalloy was heat treated for 1 hour at 1100°C plus 16 hours at 870°C. One of the samples was examined and no zones containing topologically close packed phases were found at the interface between the platinum aluminide coating and the high rhenium containing nickel based single crystal superalloy.

[0062] A high rhenium containing nickel base single crystal single crystal superalloy substrate 40 with a cobalt modified platinum aluminide coating 42 is shown in figure 5.

[0063] Some of the samples were exposed to an oxidising environment for 100 hours at 1100°C, and subsequent examination revealed no topologically close packed phases at the interface between the platinum aluminide and the high rhenium containing nickel based single crystal superalloy.

[0064] A high rhenium containing nickel base single crystal single crystal superalloy substrate 40 with a cobalt modified platinum aluminide coating 42 after exposure to an oxidising environment is shown in figure 6.

[0065] Although the present invention has referred to high rhenium containing nickel based single crystal superalloys the invention is also applicable to any high rhenium containing nickel based superalloys.

[0066] Although the invention has referred to platinum aluminide coatings the invention is also applicable to other platinum-group metal aluminide coatings, for example palladium aluminide, rhodium aluminide or combinations of these platinum-group metal aluminide coatings.

[0067] The invention is also applicable to the production of platinum-group metal aluminide bond coatings on high rhenium containing nickel based superalloys for ceramic thermal barrier coatings, for example plasma sprayed, or PVD, ceramic thermal barrier coatings.

[0068] Although the invention has referred to platinum aluminide coatings the invention is also applicable to platinum aluminide-silicide coatings, aluminide-silicide coatings and simple aluminide coatings or other suitable aluminide coatings.

[0069] In the case of the platinum aluminide-silicide coatings the surface of the high rhenium containing single crystal superalloy is modified by applying the chromium or cobalt and heat treating before application of the platinum aluminide-silicide coating.

[0070] In the case of the aluminide-silicide coatings and aluminide coatings the surface of the high rhenium

containing superalloy is modified by applying the chromium or cobalt and heat treating before application of the aluminide coating or aluminide-silicide coating.

Claims

1. A method of aluminising a high rhenium containing superalloy substrate (30,40), the high rhenium containing superalloy comprises at least 3.5wt% rhenium, the method comprising the steps of:

- (a) modifying the surface of the high rhenium containing superalloy substrate (30,40) by applying a layer of chromium or cobalt to the surface of the high rhenium containing superalloy substrate (30,40) and heat treating to diffuse the chromium or cobalt into the high rhenium containing superalloy substrate (30,40) to reduce the rhenium content of the surface of the high rhenium containing superalloy substrate (30,40), and
- (b) aluminising the high rhenium containing superalloy substrate (30,40) to form an aluminide coating (32).

2. A method as claimed in claim 1 wherein step (a) comprises applying the chromium or cobalt to the high rhenium containing superalloy substrate (30,40) by electroplating, sputtering, pack diffusion, out of pack diffusion, CVD or PVD.

3. A method as claimed in claim 1 or claim 2 wherein step (a) comprises heat treating at a temperature in the range of 900°C to 1150°C for 1 to 4 hours.

4. A method as claimed in claim 1 wherein step (a) comprises applying a layer of cobalt to a thickness of 2.5 to 12.5 micrometers to the high rhenium containing superalloy substrate (40) by electroplating and heat treating at a temperature in the range of 900°C to 1150°C for 1 to 4 hours.

5. A method as claimed in claim 1 wherein step (a) comprises chromising the surface of the high rhenium containing superalloy substrate (30) at a temperature of 1100°C for 3 hours.

6. A method as claimed in any of claims 1 to 5 wherein step (b) comprises aluminising at a temperature in the range 700°C to 1150°C.

7. A method as claimed in any of claims 1 to 6 wherein step (b) comprises pack aluminising, out of pack gas phase aluminising, chemical vapour deposition or slurry aluminising.

8. A method as claimed in any of claims 1 to 7 wherein

the high rhenium containing superalloy substrate (30,40) comprises 4 to 8 wt% rhenium.

9. A method as claimed in claim 8 wherein the high rhenium containing superalloy substrate (30,40) is nickel based.

10. A method as claimed in claim 8 or claim 9 wherein the high rhenium containing superalloy substrate (30,40) comprises 3.5 to 6.5 wt% tungsten, 2.0 to 5.0 wt% cobalt, 1.8 to 3.0 wt% chromium, 5.5 to 6.5 wt% rhenium, 5.3 to 6.5 wt% aluminium, 8.0 to 10.0 wt% tantalum, 0.2 to 0.8 wt% titanium, 0.25 to 1.5 wt% molybdenum, 0 to 0.03 wt% niobium, 0.02 to 0.05 wt% hafnium, 0 to 0.04 wt% carbon and a balance of nickel plus incidental impurities.

11. A method as claimed in any of claims 1 to 10 comprising after step (a) and before step (b) the additional steps of:

- (c) applying a layer of platinum-group metal to the modified surface of the high rhenium containing superalloy substrate (30,40),

- (d) heat treating the platinum-group metal coated high rhenium containing superalloy substrate (30,40) to diffuse the platinum-group metal into the high rhenium containing superalloy substrate (30,40),

and after step (b) the additional step of:

- (e) heat treating the aluminised, platinum-group metal coated high rhenium containing superalloy substrate (30,40) to form a platinum-group metal aluminide coating (32).

12. A method as claimed in claim 11 wherein step (c) comprises applying a layer of platinum-group metal by electroplating, sputtering, CVD or PVD to a thickness between 2.5 micrometers and 12.5 micrometers.

13. A method as claimed in claim 11 or claim 12 wherein step (c) comprises applying a layer of platinum.

14. A method as claimed in claim 11, claim 12 or claim 13 wherein step (c) comprises heat treating at a temperature in the range of 900°C to 1150°C for 1 to 4 hours.

15. A method as claimed in any of claims 11 to 14 comprising the additional step (f) of depositing a ceramic thermal barrier coating on the platinum-group metal aluminide coating (32).

16. A method as claimed in claim 15 wherein the depositing of the ceramic thermal barrier coating is by plasma spraying or PVD.

17. A method as claimed in any of claims 1 to 14 wherein step (b) comprises diffusing silicon into the high rhenium containing superalloy substrate during the aluminising step to form an aluminide-silicide coating.
18. A method as claimed in claim 17 comprising depositing a slurry containing elemental aluminium and silicon powders and heat treating to diffuse the aluminium and silicon into the high rhenium containing superalloy substrate.
19. A method as claimed in claim 18 comprising repeatedly depositing a slurry containing elemental aluminium and silicon powders and heat treating to diffuse the aluminium and silicon into the high rhenium containing superalloy substrate.
20. A method as claimed in claim 11 comprising diffusing silicon into the high rhenium containing superalloy substrate during step (b) or during step (d) to form an aluminide-silicide coating.
21. A method as claimed in claim 20 comprising depositing a slurry containing elemental aluminium and silicon powders and heat treating to diffuse the aluminium and silicon into the high rhenium containing superalloy substrate.
22. A method as claimed in claim 21 comprising repeatedly depositing a slurry containing elemental aluminium and silicon powders and heat treating to diffuse the aluminium and silicon into the high rhenium containing superalloy substrate.
23. A superalloy article having an aluminide coating obtainable by the method in any of claims 1 to 22.

Patentansprüche

1. Verfahren zur Aluminisierung eines Superlegierungs-Substrats (30, 40) mit hohem Rheniumgehalt, wobei die Superlegierung mit hohem Rheniumgehalt wenigstens 3,5 Gewichtsprozent Rhenium enthält, und wobei das Verfahren die folgenden Schritte aufweist:

(a) es wird die Oberfläche des Superlegierungs-Substrats (30, 40) mit hohem Rheniumgehalt dadurch modifiziert, daß eine Schicht aus Chrom oder Kobalt auf die Oberfläche des Superlegierungs-Substrats (30, 40) mit hohem Rheniumgehalt aufgetragen wird und eine Wärmebehandlung durchgeführt wird, um Chrom oder Kobalt in das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt diffundieren zu lassen, und um dadurch den Rhe-

niumgehalt der Oberfläche des Superlegierungs-Substrats (30, 40) mit hohem Rheniumgehalt zu reduzieren, und

(b) es wird das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt aluminisiert, um einen Aluminid-Überzug (32) zu schaffen.

2. Verfahren nach Anspruch 1, bei welchem der Schritt (a) dadurch bewirkt wird, daß Chrom oder Kobalt auf das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt durch Elektroplattierung, durch Sputtering, durch Pack-Diffusion, durch packfreie Diffusion, durch ein CVD-Verfahren oder durch ein PVD-Verfahren aufgebracht wird.
3. Verfahren nach den Ansprüchen 1 oder 2, bei welchem der Schritt (a) eine Wärmebehandlung bei einer Temperatur in dem Bereich zwischen 900° C und 1150° C während einer Zeitdauer von 1 bis 4 Stunden umfaßt.
4. Verfahren nach Anspruch 1, bei welchem mit dem Schritt (a) eine Schicht aus Kobalt in einer Dicke zwischen 2,5 und 12,5 Mikrometer auf das Superlegierungs-Substrat (40) mit hohem Rheniumgehalt durch Elektroplattierung aufgetragen wird und die Wärmebehandlung mit einer Temperatur im Bereich zwischen 900° C bis 1150° C für 1 bis 4 Stunden durchgeführt wird.
5. Verfahren nach Anspruch 1, bei welchem in dem Schritt (a) die Oberfläche des Superlegierungs-Substrats (30) mit hohem Rheniumgehalt bei einer Temperatur von 1100° C für 3 Stunden chromisiert wird.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei welchem im Schritt (b) die Aluminisierung bei einer Temperatur in dem Bereich zwischen 700° C und 1150° C durchgeführt wird.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei welchem im Schritt (b) eine Pack-Aluminisierung, eine packfreie Gas-Phasen-Aluminisierung, eine chemische Dampfablagerung oder eine Schlam-Aluminisierung durchgeführt wird.
8. Verfahren nach einem der Ansprüche 1 bis 7, bei welchem das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt 4 bis 8 Gewichtsprozent Rhenium enthält.
9. Verfahren nach Anspruch 8, bei welchem das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt eine auf Nickel basierende Superlegierung ist.

10. Verfahren nach den Ansprüchen 8 oder 9, bei welchem das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt 3,5 bis 6,5 Gewichtsprozent Wolfram, 2,0 bis 5,0 Gewichtsprozent Kobalt, 1,8 bis 3,0 Gewichtsprozent Chrom, 5,5 bis 6,5 Gewichtsprozent Rhenium, 5,3 bis 6,5 Gewichtsprozent Aluminium, 8,0 bis 10,0 Gewichtsprozent Tantal, 0,2 bis 0,8 Gewichtsprozent Titan, 0,25 bis 1,5 Gewichtsprozent Molybden, 0 bis 0,03 Gewichtsprozent Niob, 0,02 bis 0,05 Gewichtsprozent Hafnium, 0 bis 0,04 Gewichtsprozent Kohlenstoff und als Rest Nickel plus zufällige Verunreinigungen enthält.
11. Verfahren nach einem der Ansprüche 1 bis 10, bei welchem nach Durchführung des Schrittes (a) und vor Durchführung des Schrittes (b) die folgenden zusätzlichen Schritte durchgeführt werden:
- (c) es wird eine Schicht aus einem Metall der Platin-Gruppe auf die modifizierte Oberfläche des Superlegierungs-Substrats (30, 40) mit hohem Rheniumgehalt aufgetragen,
- (d) es wird das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt und dem Überzug aus dem Metall der Platin-Gruppe einer Wärmebehandlung unterworfen, um das Metall der Platin-Gruppe in das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt diffundieren zu lassen, und wobei nach dem Schritt (b) der folgende zusätzliche Schritt durchgeführt wird:
- (e) es wird das Superlegierungs-Substrat (30, 40) mit hohem Rheniumgehalt und dem Überzug aus einem Metall der Platin-Gruppe mit Wärme behandelt und aluminisiert, um einen Metall-Aluminid-Überzug (32) mit einem Metall der Platin-Gruppe zu schaffen.
12. Verfahren nach Anspruch 11, bei welchem im Schritt (c) eine Schicht aus einem Metall der Platin-Gruppe durch Elektroplattierung, Sputtering, durch ein CVD-Verfahren oder ein PVD-Verfahren bis zu einer Dicke zwischen 2,5 Mikrometer und 12,5 Mikrometer aufgetragen wird.
13. Verfahren nach den Ansprüchen 11 oder 12, bei welchem im Schritt (c) eine Schicht aus Platin aufgetragen wird.
14. Verfahren nach den Ansprüchen 11, 12 oder 13, bei welchem im Schritt (c) eine Wärmebehandlung bei einer Temperatur im Bereich zwischen 900° C und 1150° C für 1 bis 4 Stunden durchgeführt wird.
15. Verfahren nach einem der Ansprüche 11 bis 14, welches den zusätzlichen Schritt (f) umfaßt, mit dem ein keramischer thermischer Barrieren-Überzug auf dem Platin-Gruppen-Metall-Aluminid-Überzug (32) aufgetragen wird.
16. Verfahren nach Anspruch 15, bei welchem die Ablagerung des keramischen thermischen Barriere-Überzugs durch Plasma-Spritzen oder ein PVD-Verfahren erfolgt.
17. Verfahren nach einem der Ansprüche 1 bis 14, bei welchem im Schritt (b) Silizium während des Aluminisierungs-Schrittes in das Superlegierungs-Substrat mit hohem Rheniumgehalt diffundiert, um einen Aluminid-Silizid-Überzug zu erzeugen.
18. Verfahren nach Anspruch 17, bei welchem ein elementares Aluminiumpulver und Siliziumpulver enthaltender Brei abgelagert und einer Wärmebehandlung unterworfen wird, damit Aluminium und Silizium in das Superlegierungs-Substrat mit hohem Rheniumgehalt diffundieren können.
19. Verfahren nach Anspruch 18, bei welchem wiederholt ein elementares Aluminiumpulver und Siliziumpulver enthaltender Brei abgelagert und einer Wärmebehandlung unterworfen wird, damit Aluminium und Silizium in das Superlegierungs-Substrat mit hohem Rheniumgehalt diffundieren können.
20. Verfahren nach Anspruch 11, bei welchem während des Schrittes (b) oder während des Schrittes (d) Silizium in das Superlegierungs-Substrat mit hohem Rheniumgehalt diffundiert, um einen Aluminid-Silizid-Überzug zu schaffen.
21. Verfahren nach Anspruch 20, bei welchem ein elementares Aluminiumpulver und Siliziumpulver enthaltender Brei abgelagert und einer Wärmebehandlung unterworfen wird, damit Aluminium und Silizium in das Superlegierungs-Substrat mit hohem Rheniumgehalt diffundieren können.
22. Verfahren nach Anspruch 21, bei welchem wiederholt ein elementares Aluminiumpulver und Siliziumpulver enthaltender Brei abgelagert und einer Wärmebehandlung unterworfen wird, damit Aluminium und Silizium in das Superlegierungs-Substrat mit hohem Rheniumgehalt diffundieren können.
23. Aus einer Superlegierung bestehender Gegenstand mit einem Aluminid-Überzug, hergestellt durch das Verfahren nach einem der Ansprüche 1 bis 22.

Revendications

1. Procédé d'aluminisation d'un substrat de superal-

liage à haute teneur en rhénium (30, 40), le superalliage à haute teneur en rhénium comprenant au moins 3,5 % en poids de rhénium, le procédé comprenant les étapes de :

- (a) modifier la surface du substrat de superalliage à haute teneur en rhénium (30, 40) en appliquant une couche de chrome ou de cobalt sur la surface du substrat de superalliage à haute teneur en rhénium (30, 40) et le traiter thermiquement pour faire diffuser le chrome ou le cobalt dans le substrat de superalliage à haute teneur en rhénium (30, 40) pour réduire la teneur en rhénium de la surface du substrat de superalliage à haute teneur en rhénium (30, 40), et
 - (b) aluminiser le substrat de superalliage à haute teneur en rhénium (30, 40) pour former un revêtement d'aluminure (32).
2. Procédé selon la revendication 1, dans lequel l'étape (a) comprend d'appliquer le chrome ou le cobalt sur le substrat de superalliage à haute teneur en rhénium (30, 40) par électro-plaquage, vaporisation sous vide, diffusion en paquet, diffusion hors paquet, déposition en phase gazeuse par procédé chimique ou déposition en phase gazeuse par procédé physique.
 3. Procédé selon la revendication 1 ou 2, dans lequel l'étape (a) comprend de traiter thermiquement à une température de l'ordre de 900°C à 1150°C pendant 1 à 4 heures.
 4. Procédé selon la revendication 1, dans lequel l'étape (a) comprend d'appliquer une couche de cobalt avec une épaisseur de 2,5 à 12,5 micromètres sur le substrat de superalliage à haute teneur en rhénium (40) par électro-plaquage et de traiter thermiquement à une température de l'ordre de 900°C à 1150°C pendant 1 à 4 heures.
 5. Procédé selon la revendication 1, dans lequel l'étape (a) comprend de chromer la surface du substrat de superalliage à haute teneur en rhénium (30) à une température de 1100°C pendant 3 heures.
 6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'étape (b) comprend d'aluminiser à une température de l'ordre de 700°C à 1150°C.
 7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'étape (b) comprend d'aluminiser en paquet, d'aluminiser hors paquet en phase gazeuse, de déposer en phase vapeur par procédé chimique ou d'aluminiser par coulis.
 8. Procédé selon l'une quelconque des revendications

1 à 7, dans lequel le substrat de superalliage à haute teneur en rhénium (30, 40) comprend 4 à 8 % en poids de rhénium.

9. Procédé selon la revendication 8, dans lequel le substrat de superalliage à haute teneur en rhénium (30, 40) est à base de nickel.
10. Procédé selon la revendication 8 ou 9, dans lequel le substrat de superalliage à haute teneur en rhénium (30, 40) comprend 3,5 à 6,5 % en poids de tungstène, 2,0 à 5,0 % en poids de cobalt, 1,8 à 3,0 % en poids de chrome, 5,5 à 6,5 % en poids de rhénium, 5,3 à 6,5 % en poids d'aluminium, 8,0 à 10,0 % en poids de tantale, 0,2 à 0,8 % en poids de titane, 0,25 à 1,5 % en poids de molybdène, 0 à 0,03 % en poids de niobium, 0,02 à 0,05 % en poids d'hafnium, 0 à 0,04 % en poids de carbone et le reste de nickel plus des impuretés incidentes.
11. Procédé selon l'une quelconque des revendications 1 à 10 comprenant après l'étape (a) et avant l'étape (b) les étapes additionnelles de :
 - (c) appliquer une couche de métal du groupe du platine sur la surface modifiée du substrat de superalliage à haute teneur en rhénium (30, 40),
 - (d) traiter thermiquement le substrat de superalliage à haute teneur en rhénium (30, 40) revêtu de métal du groupe du platine pour faire diffuser le métal du groupe du platine dans le substrat de superalliage à haute teneur en rhénium (30, 40),
 - et après l'étape (b) l'étape additionnelle de :
 - (e) traiter thermiquement le substrat de superalliage à haute teneur en rhénium (30, 40) revêtu de métal du groupe du platine aluminisé pour former un revêtement d'aluminure de métal du groupe du platine (32).
12. Procédé selon la revendication 11, dans lequel l'étape (c) comprend d'appliquer une couche de métal du groupe du platine par électro-plaquage, vaporisation sous vide, déposition en phase vapeur par procédé chimique ou déposition en phase vapeur par procédé physique avec une épaisseur située entre 2,5 micromètres et 12,5 micromètres.
13. Procédé selon la revendication 11 ou 12, dans lequel l'étape (c) comprend d'appliquer une couche de platine.
14. Procédé selon la revendication 11, 12 ou 13, dans lequel l'étape (c) comprend de traiter thermiquement à une température de l'ordre de 900°C à 1150°C pendant 1 à 4 heures.

15. Procédé selon l'une quelconque des revendications 11 à 14 comprenant l'étape additionnelle (f) de déposer une couche barrière thermique céramique sur le revêtement d'aluminure de métal du groupe du platine (32). 5
16. Procédé selon la revendication 15, dans lequel la déposition du revêtement de barrière thermique céramique est réalisée par pulvérisation de plasma ou déposition en phase vapeur par procédé physique. 10
17. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel l'étape (b) comprend de faire diffuser du silicium dans le substrat de superalliage à haute teneur en rhénium pendant l'étape d'aluminisation pour former un revêtement de siliciure-aluminure. 15
18. Procédé selon la revendication 17 comprenant de déposer un coulis contenant des poudres d'aluminium et de silicium élémentaires et de traiter thermiquement pour faire diffuser l'aluminium et le silicium dans le substrat de superalliage à haute teneur en rhénium. 20
25
19. Procédé selon la revendication 18 comprenant de déposer de manière répétée un coulis contenant des poudres d'aluminium et de silicium élémentaires et de traiter thermiquement pour diffuser l'aluminium et le silicium dans le substrat de superalliage à haute teneur en rhénium. 30
20. Procédé selon la revendication 11 comprenant de faire diffuser du silicium dans le substrat de superalliage à haute teneur en rhénium pendant l'étape (b) ou pendant l'étape (d) pour former un revêtement d'aluminure-siliciure. 35
21. Procédé selon la revendication 20 comprenant de déposer un coulis contenant des poudres d'aluminium et de silicium élémentaires et de traiter thermiquement pour faire diffuser l'aluminium et le silicium dans le substrat de superalliage à haute teneur en rhénium. 40
45
22. Procédé selon la revendication 21 comprenant de déposer de manière répétée un coulis contenant des poudres d'aluminium et de silicium élémentaires et de traiter thermiquement pour diffuser l'aluminium et le silicium dans le substrat de superalliage à haute teneur en rhénium. 50
23. Article en superalliage ayant un revêtement d'aluminure obtenu par le procédé selon l'une quelconque des revendications 1 à 22. 55

Fig.1.

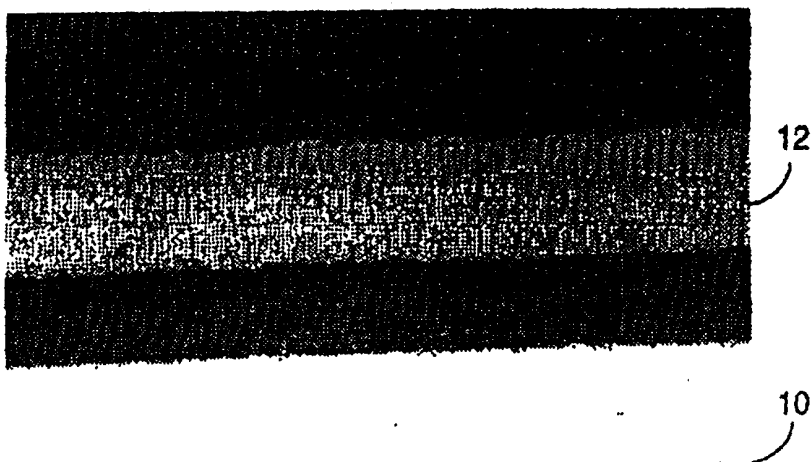


Fig.2.

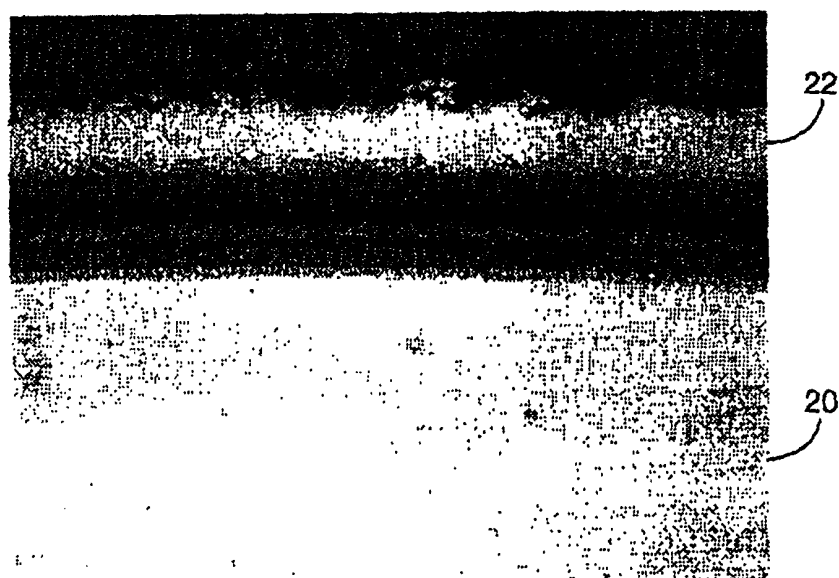


Fig.3.

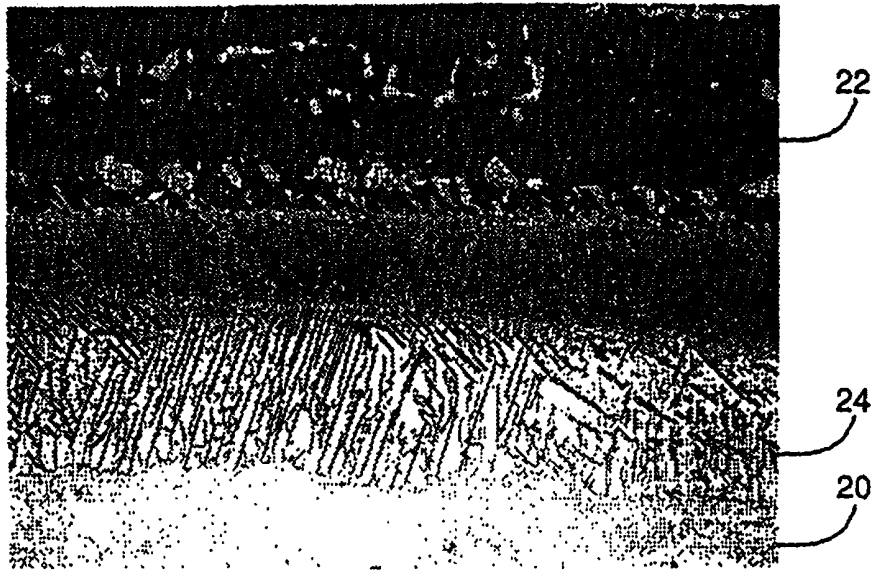


Fig.4.

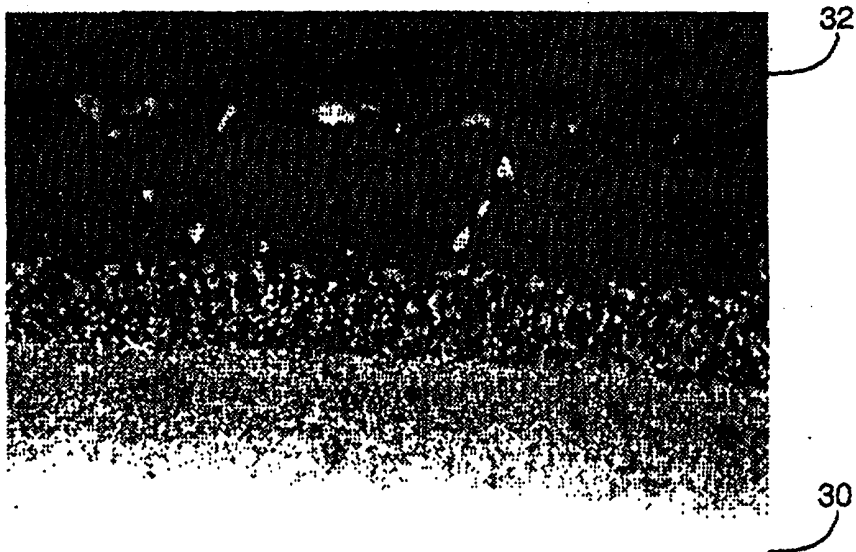


Fig.5.

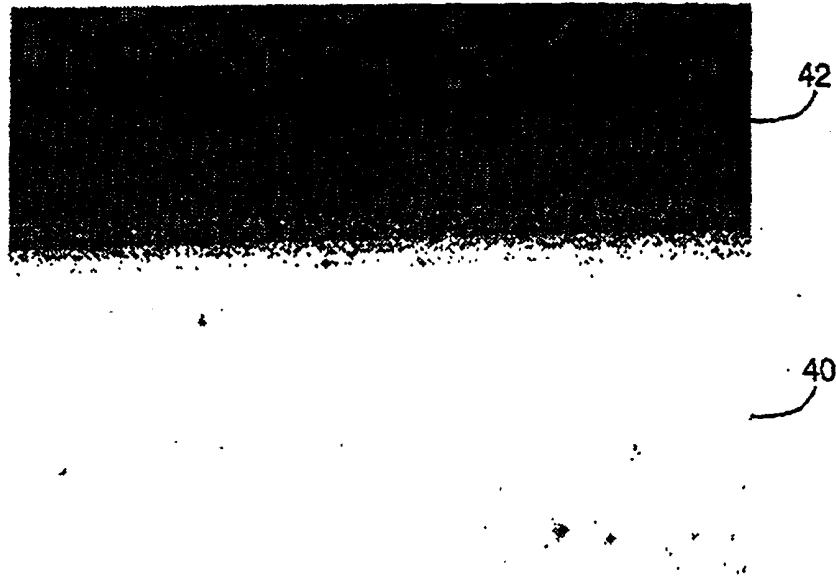


Fig.6.

